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Citation	Applied Physics Letters. 76(10) p.1228-p.1230
Issue Date	2000-02-28
oaire:version	VoR
URL	<a href="https://hdl.handle.net/11094/75836">https://hdl.handle.net/11094/75836</a>
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# Photoinduced layer alignment control in ferroelectric liquid crystal with $N^*-C^*$ phase transition doped with photochromic dye

Cite as: Appl. Phys. Lett. **76**, 1228 (2000); <https://doi.org/10.1063/1.125992>

Submitted: 15 September 1999 . Accepted: 11 January 2000 . Published Online: 28 February 2000

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# Photoinduced layer alignment control in ferroelectric liquid crystal with $N^*$ – $C^*$ phase transition doped with photochromic dye

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(Received 15 September 1999; accepted for publication 11 January 2000)

Photoinduced layer alignment control has been proposed in an azo-dye-doped ferroelectric liquid crystal with a chiral nematic ( $N^*$ )–chiral smectic  $C$  ( $SmC^*$ ) phase sequence. This layer alignment control is based on the  $N^*$ – $SmC^*$  phase transition induced by the photoisomerization of the azo-dye. *Trans-cis* photoisomerization of the azo-dye upon UV irradiation in the  $SmC^*$  phase induces the  $N^*$  phase, and an opposite isomerization process upon sequentially stopping the UV irradiation induces the  $SmC^*$  phase again. The photoinduced  $SmC^*$ – $N^*$ – $SmC^*$  phase transition under an appropriate electric field allows us to control the smectic layer alignment. This photoassisted layer switching can be applied to the fabrication of the designed multidomain structure in electro-optic elements such as display, optical memory, and optical grating. © 2000 American Institute of Physics. [S0003-6951(00)02010-6]

Liquid crystal doped with a photochromic dye is expected to have favorable potentials for a variety of photonic applications. Photochromic molecules change their structures reversibly upon light irradiation, which can induce change in characteristics in the liquid crystal such as the phase transition temperature, molecular alignment, helical twisting power, spontaneous polarizations, and so on.<sup>1–4</sup> These optically controllable characteristics can be used for functional photonic elements such as optical detectors, switches, and recorders.

On the other hand, ferroelectric liquid crystals (FLCs) have excellent characteristics for electro-optic applications such as a quick response caused by the direct interaction between spontaneous polarization ( $P_s$ ) and an electric field, and a memory effect in a thin cell. So far, however, FLC having a chiral nematic ( $N^*$ )–chiral smectic  $C$  ( $SmC^*$ ) phase sequence (NC-FLC) has been considered not to be favorable for application to display devices. In NC-FLC, the smectic layer normal in the  $SmC^*$  phase does not coincide with the alignment (rubbing) axis in a sandwich cell with a conventional rubbing treatment, and there are two types of layer arrangements whose layer normals make angles of  $\pm\theta$  (tilt angle) with respect to the rubbing axis (Fig. 1). In such a cell, the electro-optic response is monostable, so that few studies on display device application have been carried out using NC-FLC.<sup>5</sup> However, NC-FLC has interesting characteristics as a candidate as an electro-optic element.<sup>6–8</sup> Myojin *et al.* have reported the alignment control of NC-FLC upon application of an ac electric field in the cell in which both substrate surfaces have been rubbed.<sup>7</sup> On the other hand, Nakayama, Ozaki, and Yoshino have reported a rewritable optical recording in NC-FLC using a thermal process due to laser irradiation.<sup>8</sup> In this study, we propose photoassisted control of smectic layer alignment in an azo-dye-doped NC-FLC.

Figure 2 shows the molecular structures of the liquid

crystal, chiral dopant, and azo-dye used in this study. An achiral smectic- $C$  liquid crystal, 4-hexyloxyphenyl 4-octyloxybenzoate (HOPOOB), doped with a chiral molecule (S811, Merk) of 1 wt % concentration, was used for the NC-FLC. 4-diethylaminoazobenzene was doped as a photochromic azo-dye. The absorption spectra of this dye in a hexane solution are shown in Fig. 3. The original absorption spectrum before UV irradiation is indicated by a solid line. The concentration of the azo-dye in the FLC was varied from 3 to 7 wt %. These mixtures show an isotropic- $N^*$ – $SmC^*$  phase sequence.

The sample was filled by a capillary action into a sandwich cell, which consists of two indium–tin–oxide (ITO)-coated glass plates. The cell gap was 2  $\mu\text{m}$ . In such a thin cell no texture due to the helix was observed. To obtain a homogeneously aligned cell, the surfaces were coated with a polyimide (AL1254, Japan Synthetic Rubber) and rubbed in the antiparallel direction to each other. The sample was set between crossed polarizers and observed by a polarizing optical microscope. The texture was recorded using a charge-coupled device digital camera (HC-300, FUJIFILM).

The temperature of the sample was controlled using a

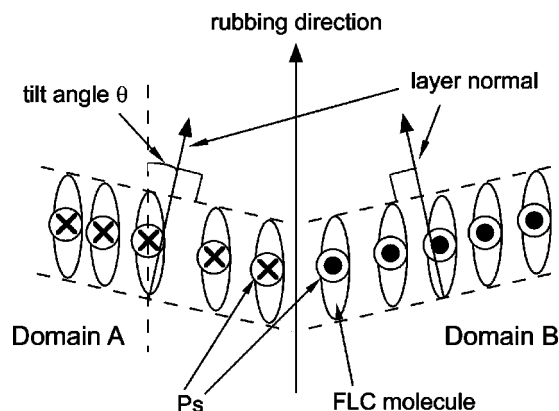


FIG. 1. Two possibilities of layer arrangements in the  $SmC^*$  phase of NC-FLC.

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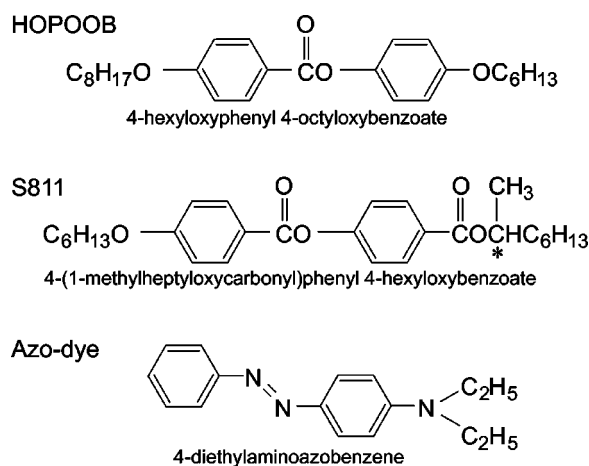


FIG. 2. Molecular structures of achiral liquid crystal, chiral dopant, and azo-dye.

hot bath and a temperature controller (FP21, SHIMADEN). Light illumination was performed by a 160 W metal-halide lamp (IMH-160, SIGMA KOKI). In order to induce *trans-cis* photoisomerization of the azo-dye, a UV pass filter C-40C (TOSHIBA) was installed in front of the sample, which transmitted light having a wavelength region from 280 to 420 nm. For the observation of textures, a long-pass filter O-56 ( $>560$  nm; orange light) was used to avoid *trans-cis* photoisomerization of the azo-dye. As is evident from Fig. 3, photochromic characteristics were confirmed in the dye. Upon UV irradiation for 1 min, the absorption band around 400 nm was suppressed, as shown by the dotted line, which corresponds to the *trans-cis* photoisomerization.

Figure 4 shows the schematic explanation of the proposed photoinduced layer alignment control in the azo-dye-doped NC-FLC. As mentioned above, two kinds of layer alignments, whose layer normal make angles of  $\pm\theta$  with respect to the rubbing direction, can be formed in the  $\text{SmC}^*$  phase, as shown in Fig. 1. Upon cooling down from the  $N^*$  phase to the  $\text{SmC}^*$  phase under application of a dc electric field, however, uniform unidirectional layer alignment can be

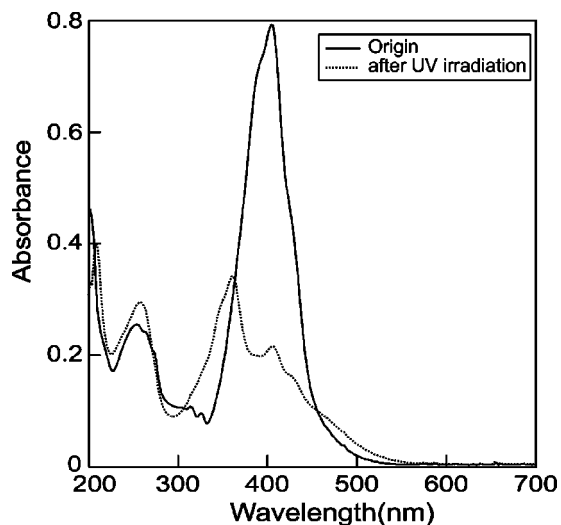


FIG. 3. Absorption spectra of 4-diethylaminoazobenzene in a hexane solution. Solid line indicates the original spectrum before UV irradiation (*trans* form), and dotted line shows the spectrum after UV irradiation for 1 min (*cis* form). The concentration of azo-dye is about  $10^{-5}$  mol/l.

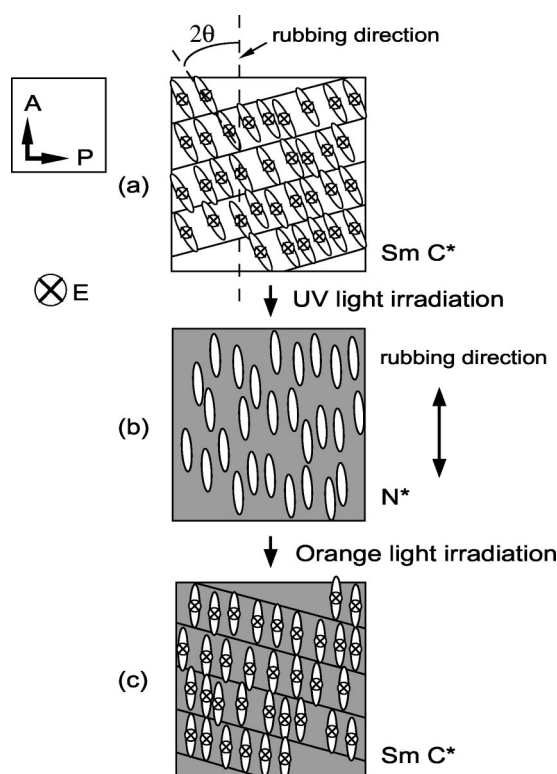


FIG. 4. Schematic explanation of the photoinduced layer switching proposed in this study.

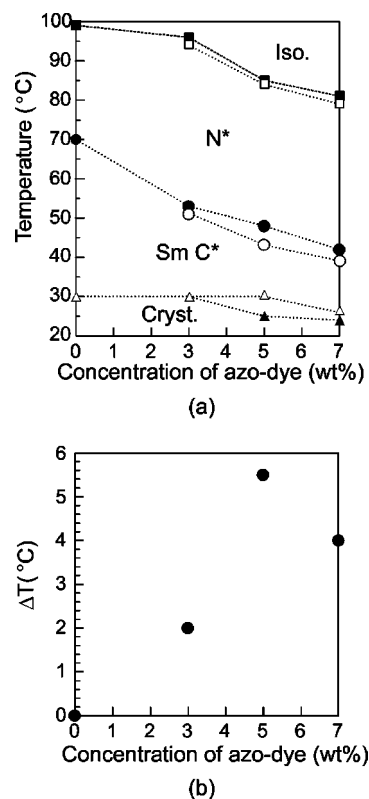


FIG. 5. (a) Phase transition temperatures of the azo-dye-doped NC-FLC in dark (closed symbols) and UV-irradiated (open symbols) states as a function of the concentration of the azo-dye. (b) Dye concentration dependence of the temperature shift of the  $N^*$ - $\text{SmC}^*$  phase transition caused by UV irradiation.

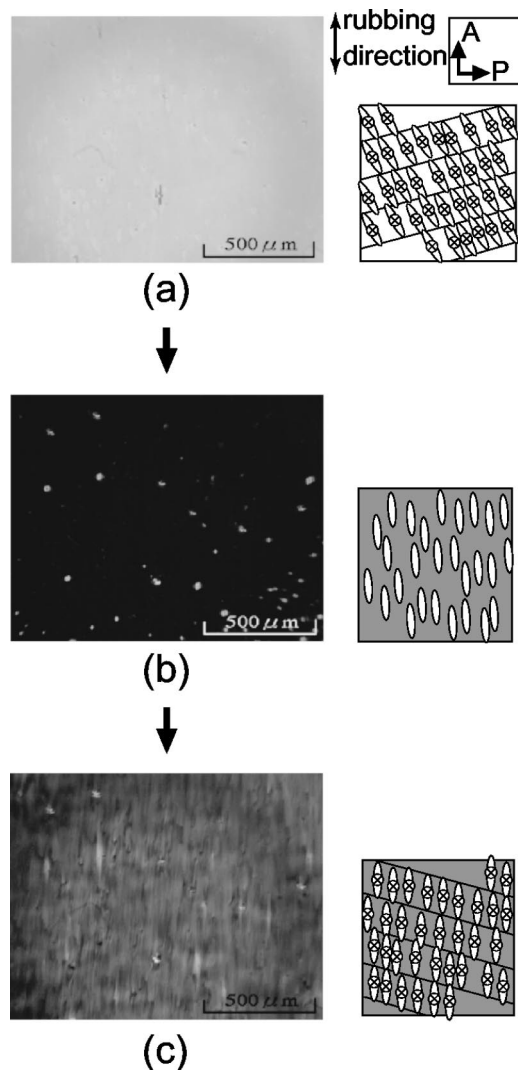


FIG. 6. Polarizing microphotographs of the dye-doped NC-FLC before and after UV irradiation. (a)  $\text{SmC}^*$  phase before UV irradiation; (b)  $N^*$  phase induced by UV irradiation; and (c)  $\text{SmC}^*$  phase after stopping UV irradiation.

realized in the entire area of the cell (e.g., domain B). When the polarity of the applied field is reversed, the molecules tilt away from the rubbing direction by  $2\theta$  [Fig. 4(a)]. In this state, if UV light is irradiated, the  $N^*$  phase is induced due to *trans-cis* photoisomerization of the azo-dye and liquid-crystal molecules tend to align along the rubbing direction, as shown in Fig. 4(b). Upon sequentially stopping UV irradiation, an opposite photoisomerization process (*cis-trans*) causes the reentrance into the  $\text{SmC}^*$  phase, keeping molecules parallel to the rubbing direction, as shown in Fig. 4(c). Consequently, another domain (domain A), in which the layer normal tilts to the opposite direction with respect to that in Fig. 4(a), can be obtained.

We have investigated the effect of the photoisomerization of azo-dye to the phase transition of the FLC. Figure 5 shows the phase transition temperatures of irradiated and nonirradiated FLC by UV light as a function of the concentration of the azo-dye. As shown in Fig. 5(a), the phase transition temperatures decrease with increasing the concentration of the azo-dye in the host FLC. It should be noted that the  $N^*-C^*$  transition temperature is lowered by the irradiation of UV light.

Figure 5(b) shows the temperature shift of the  $N^*-C^*$  phase transition caused by the UV irradiation as a function of the dye concentration. With increasing concentration of the azo-dye, the caused temperature shift increases. Namely, it is expected that as more azo-dye is doped, the more effectively it affects the phase transition temperature of the host FLC. At high concentration of the azo-dye (more than 7 wt %), however, the smectic A ( $\text{SmA}$ ) phase appears between the  $N^*$  and  $\text{SmC}^*$  phases. The study mentioned below was carried out using a sample with a dye concentration of 5 wt %.

First, the sample was heated to the isotropic phase and then cooled down to the  $\text{SmC}^*$  phase. To obtain uniform unidirectional layer alignment, a negative electric field ( $-E$ ) was applied at the phase transition from the  $N^*$  to the  $\text{SmC}^*$  phase. The temperature of the sample was kept just below the  $N^*-\text{SmC}^*$  phase transition point. One of the crossed polarizers was set parallel to the rubbing direction. To realize a bright state, the polarity of the applied field was reversed to  $+E$ , as shown in Fig. 6(a), which corresponds to the state shown in Fig. 4(a). When UV light was irradiated to the sample by changing the long-pass filter into an UV pass filter, the  $\text{SmC}^*-\text{N}^*$  phase transition was induced due to the photoisomerization of the azo-dye, and the  $N^*$  phase appeared [Fig. 6(b)]. Upon stopping the UV irradiation, the temperature reentered into the  $\text{SmC}^*$  phase, in which the smectic layer was formed again, as shown in Fig. 6(c). It should be noted that extinction is obtained in the reentered  $\text{SmC}^*$  phase in spite of the constant electric field during the light irradiation. As evident from Fig. 4, it means that the smectic layer switching was performed by the irradiation of UV light.

In this study, layer alignment control was succeeded at only  $1-3^\circ\text{C}$  below the  $N^*-C^*$  phase transition temperature. However, by selection of a more suitable dye for the purpose (such as one with high solubility, absorbability, and strong interaction between the liquid crystallinity and the photoisomerization), the temperature shift due to the photoisomerization of the dye should be more effectively induced.

In conclusion, we proposed a photoinduced layer alignment control in an azo-dye-doped ferroelectric liquid crystal with a  $N^*-\text{SmC}^*$  phase sequence. This layer alignment control was based on the  $N^*-\text{SmC}^*$  phase transition induced by the photoisomerization of the doped azo-dye. This photoassisted layer switching can be applied to the fabrication of the designed multidomain structure in electro-optical elements such as display, optical memory, and optical grating.

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